Reconnaissance Survey of Nonpoint Source Pesticides in Maryland Surface Waters

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Title: Reconnaissance Survey of Nonpoint Source Pesticides in Maryland Surface Waters

Abstract: As part of the Chesapeake Bay Agreement, the "Maryland Toxics Reduction Strategy for the Chesapeake Bay and its Tributaries" committed the State to identify the most extensively used pesticides and to select those to be included in any monitoring program. As a first step toward implementing a monitoring program, this reconnaissance level survey analyzed water from streams throughout the state for seven priority pesticides: atrazine, alachlor, carbofuran, chlorpyrifos, cyanazine, metolachlor, and simazine. Water samples were collected from 21 sites on 12 streams, ranging in size from small drainage ditches between agricultural fields to major rivers such as the Monocacy River.

All but one of the seven pesticides were detected. Metolachlor was detected most frequently in 14 of 21 sampling sites, followed by atrazine and cyanazine both occurring in 6 of 21 sites. Chlorpyrifos was detected in only one stream which was surrounded by urban and industrial development. Carbofuran was not detected in any sample, however laboratory tests showed degradation may have occurred during storage. The largest stream sampled, the Monocacy River, contained the highest number of pesticides. Only one stream, excluding control streams, contained no detectable levels of the seven pesticides.

Chlorpyrifos was the only pesticide analyzed for with established U.S. Environmental Protection Agency water quality criteria. Levels found in samples from the single stream were at or above acute and chronic criteria levels for the protection of freshwater aquatic organisms. All other pesticides detected were herbicides, and occurred at concentrations several orders of magnitude below those expected to cause toxicity to vertebrates and invertebrates. Atrazine was measured in samples from some streams at levels ranging from below detection to 2.88 µg/L. Results of other studies have indicated toxicity to photosynthetic organisms at these levels. Recommendations for future monitoring and further research are provided.

Key words: atrazine, alachlor, carbofuran, chlorpyrifos, cyanazine, metolachlor, simazine, monitoring, surface water, pesticides.

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INTRODUCTION

Vast tracts of land in Maryland and in the United States are dedicated to agriculture, and much of this acreage is treated with pesticides. Commonly used pesticides today do not have the persistence and bioaccumulation problems associated with previously used pesticides, such as DDT and the other organochlorines. However, the characteristics which reduce a pesticide's persistence and ability to accumulate also make it more water soluble. Pesticides can be washed from fields by surface water runoff and become available to fish, invertebrates, wetland plants, and other aquatic biota.

Nonpoint source contamination is difficult to assess. Pesticide input into aquatic systems is often irregular as it is associated with rain events. Many different pesticides may be used in a watershed, with different application times, rates, and physical characteristics such as water solubility and persistence. The magnitude of the problem of pesticide runoff into Maryland streams is just beginning to be assessed. Monitoring of water for most of today's pesticides is infrequent, and little is known about possible environmental effects. Of the 12 pesticides most heavily used for agriculture in Maryland (Maryland Department of Agriculture 1990), none appear on the U.S. Environmental Protection Agency (EPA) Priority Pollutant list, and only one has EPA water quality criteria. Monitoring of today's pesticides in surface waters is essential for assessing the health of aquatic ecosystems.

The Chesapeake Bay Agreement was signed in 1987 by EPA, the District of Columbia, and the States of Maryland, Virginia, and Pennsylvania, and included a commitment to enact a basinwide strategy to reduce toxics. The "Maryland Toxics Reduction Strategy for the Chesapeake Bay and its Tributaries" committed the State to identify the most extensively used pesticides, to assess methods and resources required for a monitoring program, and to select pesticides for inclusion in a monitoring program by December, 1989. The information gathered to date by the Maryland Department of Environment (MDE) has been incorporated into the design of this study.

This was a reconnaissance-level study. The objectives were to develop baseline information on which pesticides were occurring in various streams and in what quantities. The study was a collaborative effort by the U.S Fish and Wildlife Service and the Maryland Department of Environment. The U.S. Fish and Wildlife Service, Annapolis Field Office, received funding to examine the effects of pesticides on aquatic biota, and contacted MDE to explore possible cooperative efforts. MDE staff recently selected six pesticides of concern based on use, toxicity, persistence, and human health risk. U.S. Fish and Wildlife

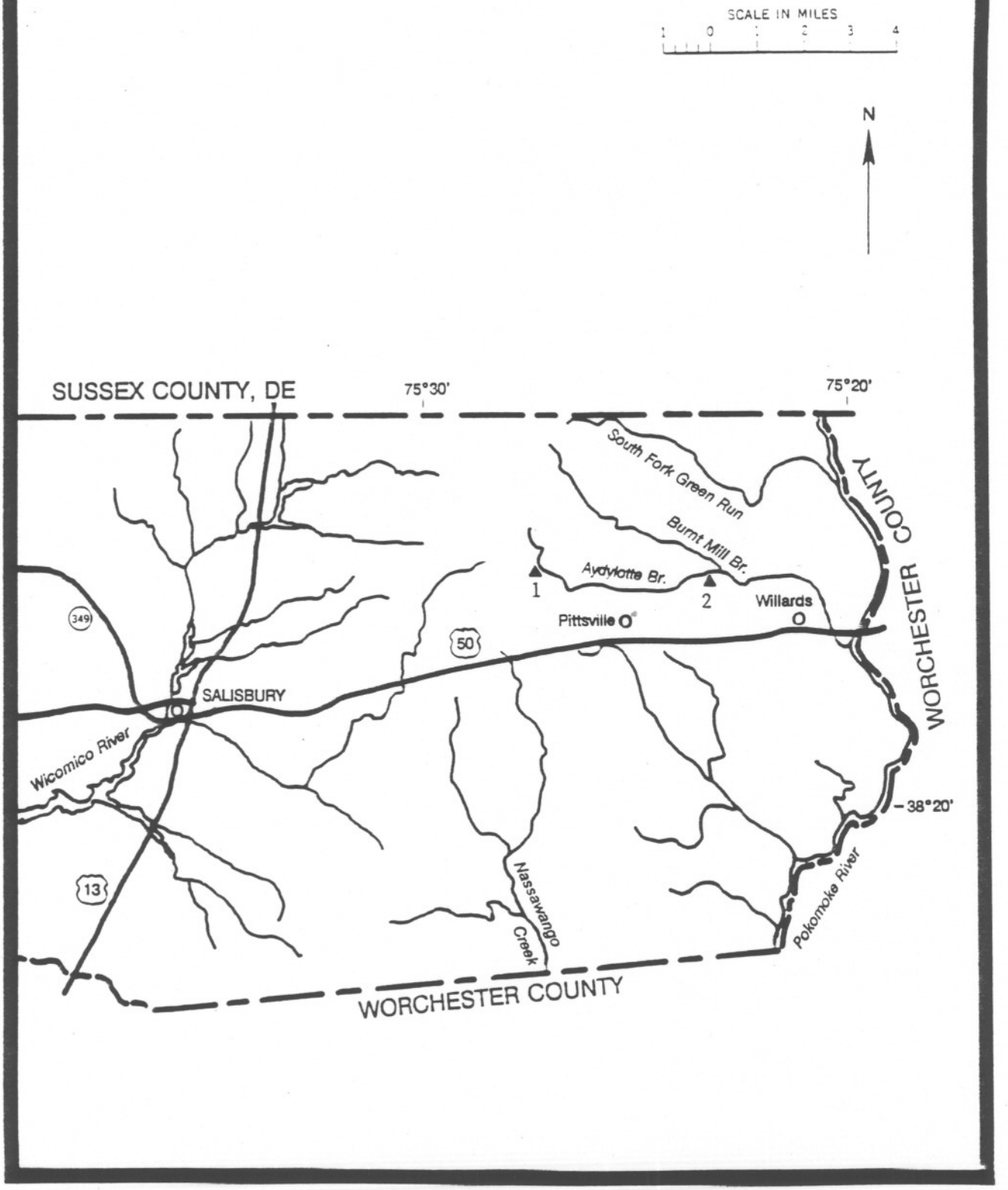
Service staff added a seventh pesticide of possible concern in a particular stream inhabited by a Federally endangered species. MDE staff developed a study plan containing sample sites in a variety of streams in agricultural, urban, and forested (control) areas, through coordination with Maryland Department of Agriculture, U.S. Geologic Survey, Maryland Department of Environment, Soil Conservation Service, and University of Maryland Extension Service. The U.S. Fish and Wildlife Service collected water samples, provided analytical and quality assurance/quality control services, and produced this report.

Seven pesticides were analyzed in samples from selected Maryland streams. Three of the pesticides are triazine herbicides: atrazine, cyanazine, and simazine. These herbicides work by inhibition of photosynthesis and are not very toxic to fish and invertebrates (Maryland Department of Environment 1989). Alachlor and metolachlor are herbicides and affect plants by inhibition of protein synthesis. These compounds are also not very toxic to animals (Maryland Department of Environment 1989). Chlorpyrifos is an organophosphate insecticide; carbofuran is a carbamate insecticide. Both act to inhibit cholinesterases, which are enzymes important in nerve impulse transmission (Maryland Department of Environment 1989). Thus, they have a much greater potential to affect both invertebrate and vertebrate nontarget organisms. These seven pesticides vary in their water solubility, affinity for particles, and tendency to bioaccumulate. Also, the possible synergistic effects to biota exposed to combinations of these seven pesticides with each other, or with or other contaminants, has not been fully explored.

METHODS AND MATERIALS

Ambient water samples were collected from selected streams throughout Maryland (Figures 1-6). Stream types ranged from small drainage ditches between agricultural fields to major rivers such as the Monocacy River. Water samples were collected from 21 sites on 12 streams during July 18-22, 1990. The number of sites per waterway ranged from one to four: six streams were sampled by a single site, three streams by two sites, two by three sites, and one by four sites. At each site, three replicate water samples were collected in pre-labelled chemically clean jars (I-Chem Research, New Castle, DE) by wading out to a depth of about two feet when possible. Jars were submerged upstream of the collector to avoid contamination of the sample with stirred up sediment. The jar was immersed slowly into the water until full and then capped. This was done to include as much of the surface microlayer as possible, as the microlayer often contains higher levels of contaminants. Three jars were filled consecutively from the same location, wrapped separately in plastic, and put on wet ice. Upon return to the field office,

Figure 1. Wicomico County, MD - surface water collection sites are represented by triangles.



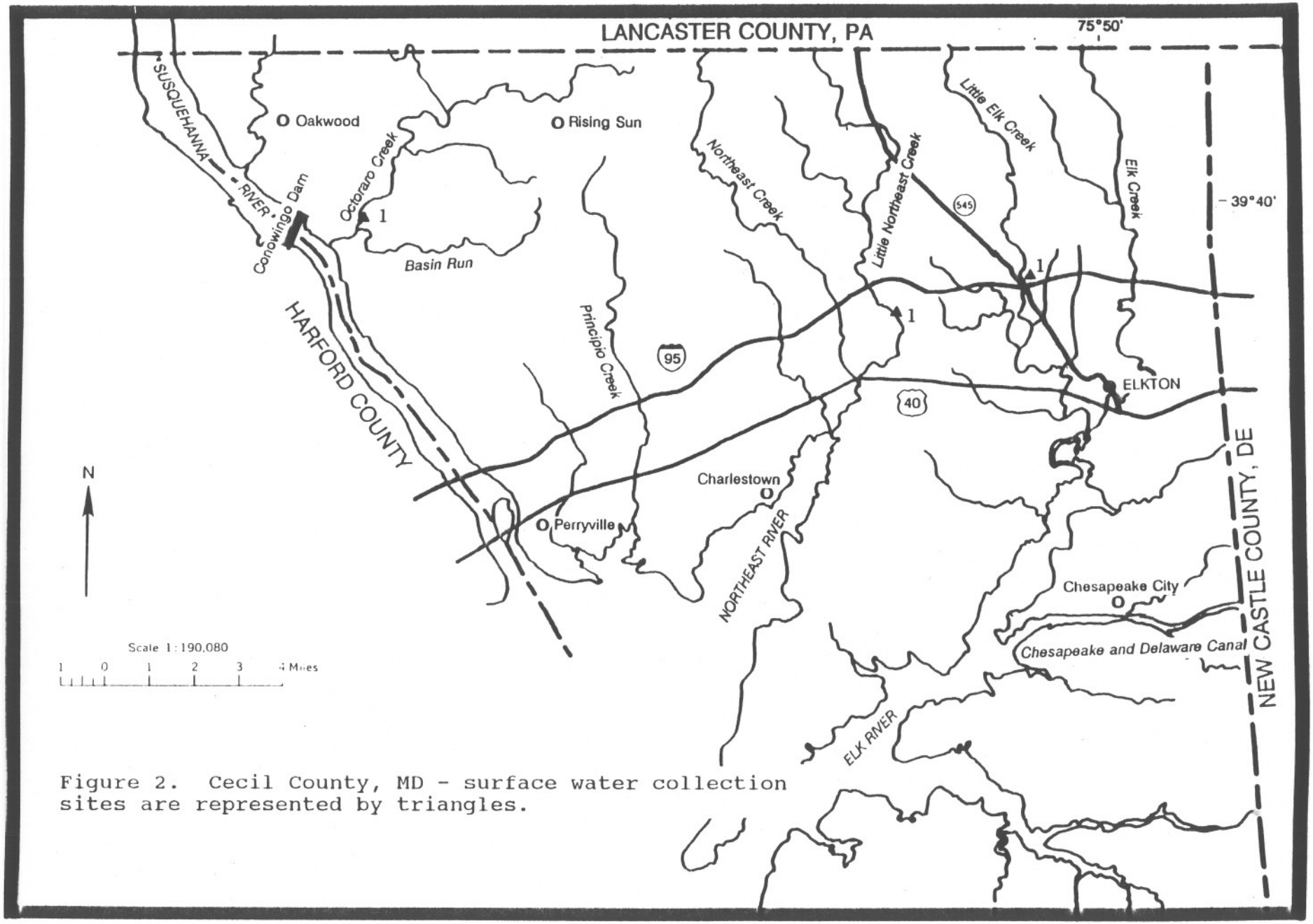


Figure 2. Cecil County, MD - surface water collection sites are represented by triangles.

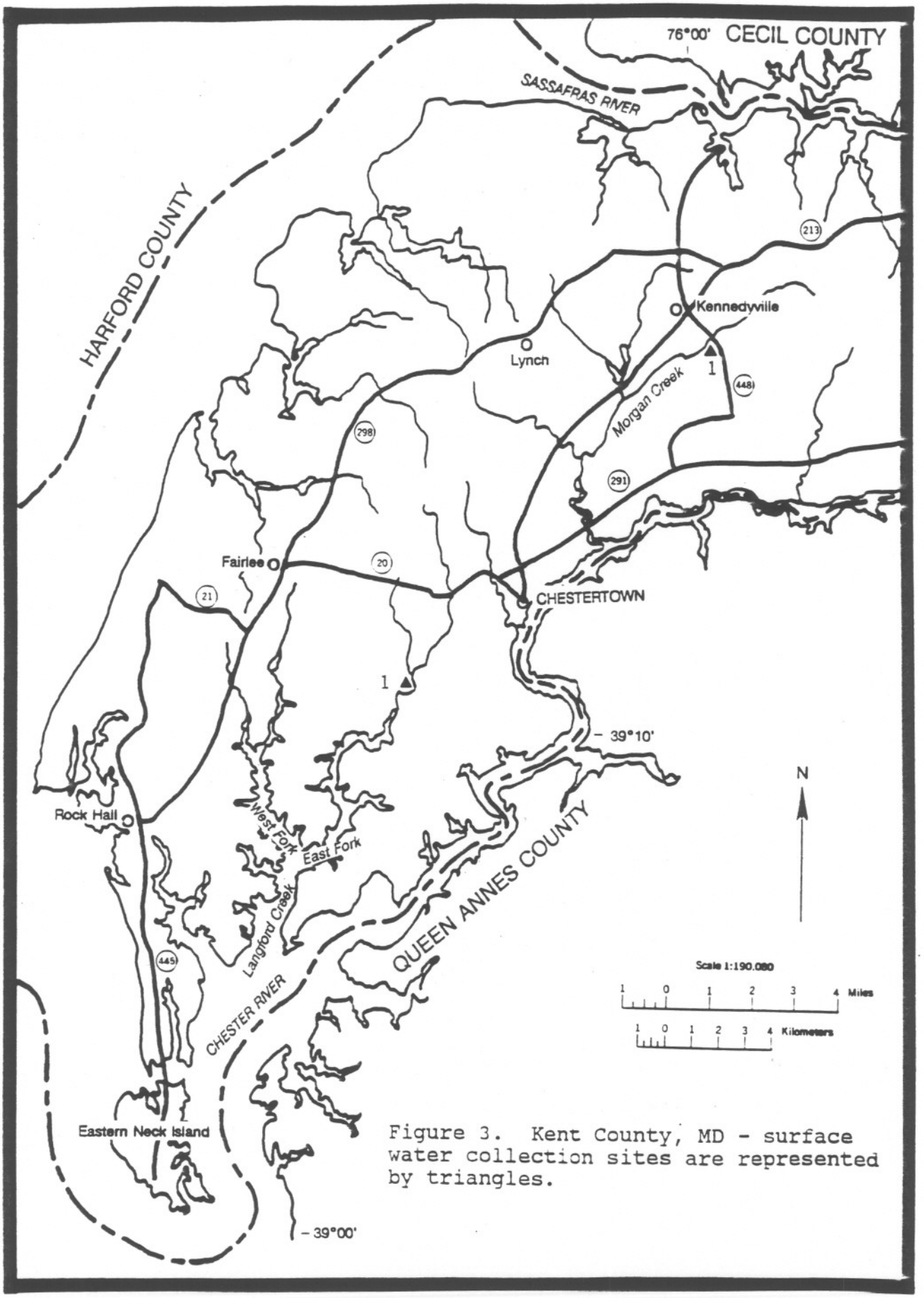


Figure 3. Kent County, MD - surface water collection sites are represented by triangles.

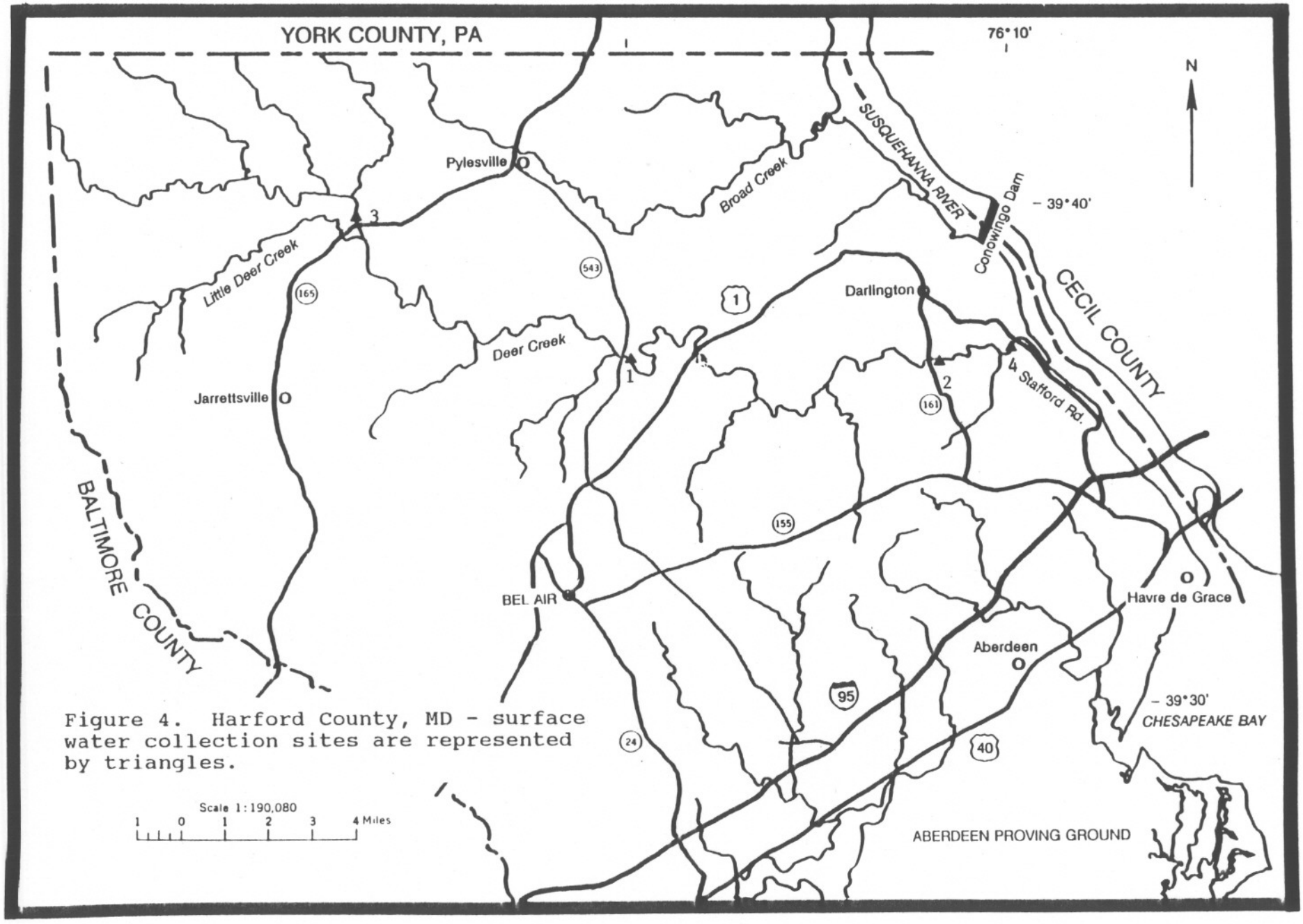
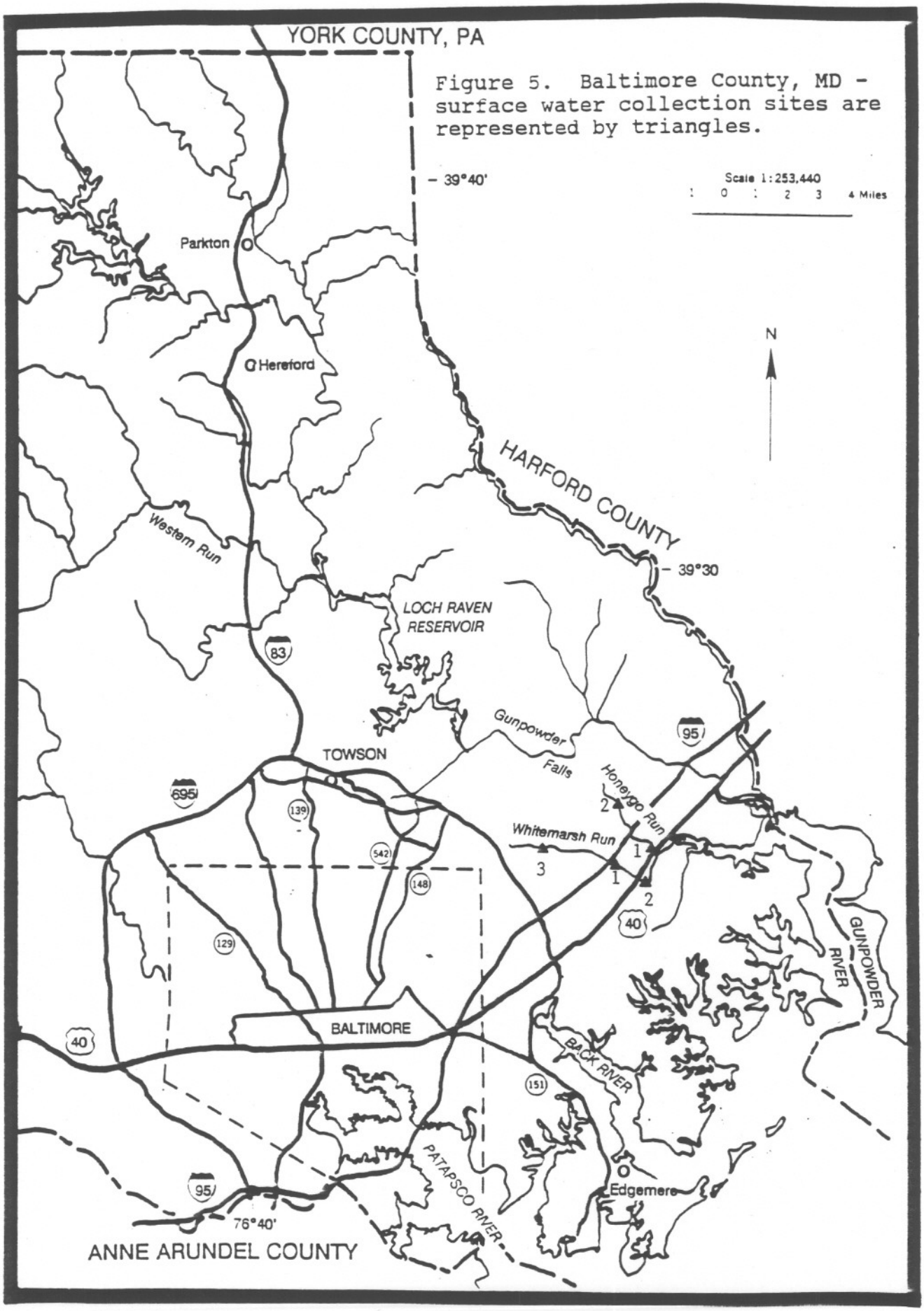


Figure 4. Harford County, MD - surface water collection sites are represented by triangles.


YORK COUNTY, PA
Figure 5. Baltimore County, MD - surface water collection sites are represented by triangles.
39°40'
Scale 1:253,440
1 0 1 2 3 4 Miles
N
Parkton
Hereford
HARFORD COUNTY
39°30
Western Run
LOCH RAVEN RESERVOIR
83
Gunpowder Falls
95
TOWSON
695
139
Honeygo Run
2
Whitemarsh Run
3
1
1
2
542
148
40
129
GUNPOWDER RIVER
BALTIMORE
40
BACK RIVER
151
PATAPSCO RIVER
95
Edgemere
76°40'
ANNE ARUNDEL COUNTY

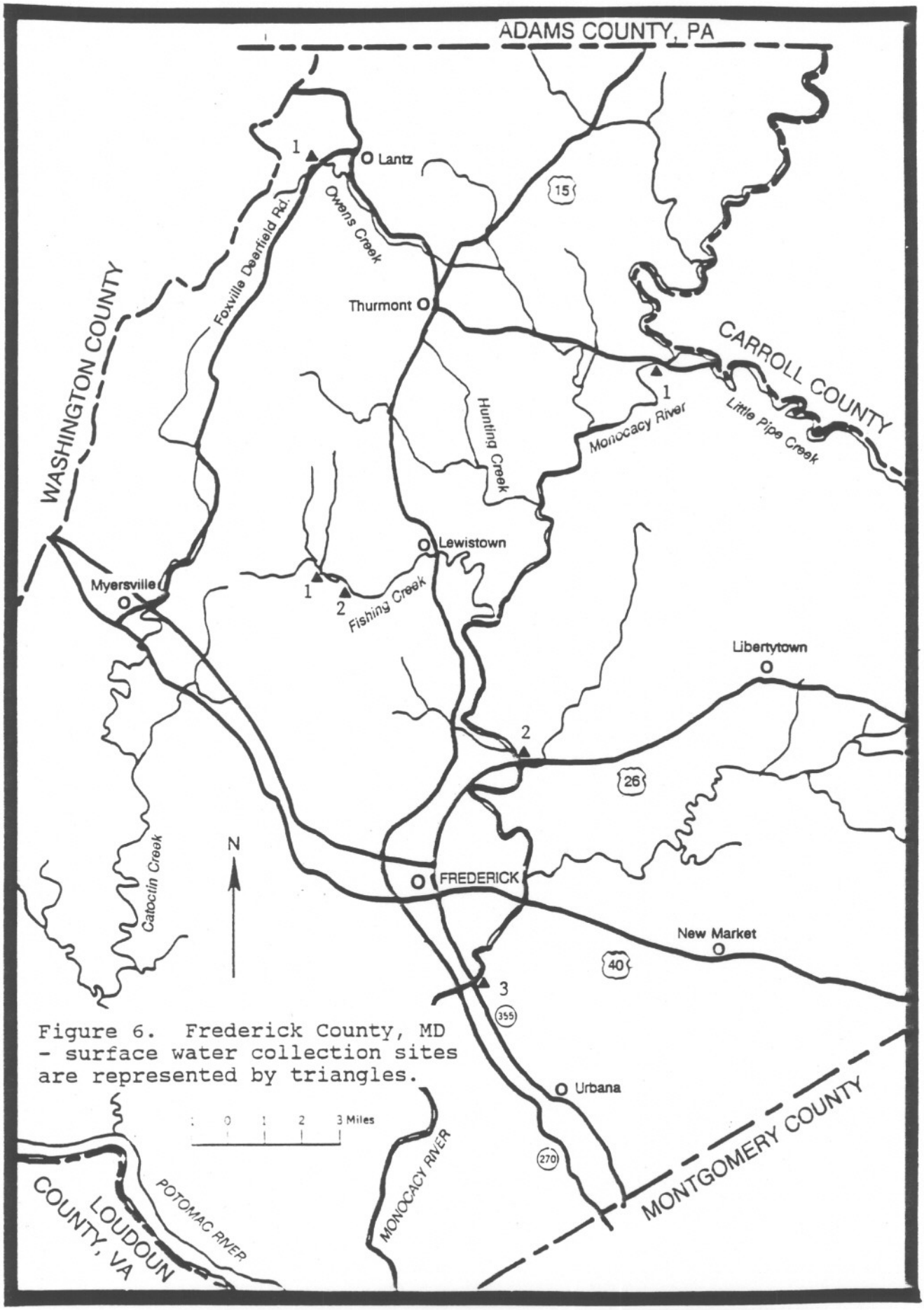


Figure 6. Frederick County, MD - surface water collection sites are represented by triangles.

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samples were placed in a 4°C refrigerator. During storage, a few jars which were in contact with the refrigerator coils became partially frozen.

For shipping, each sample jar was wrapped in bubble wrap and placed in a cooler with wet ice. Samples were shipped to Mississippi State Chemical Laboratory, Mississippi State University, on July 23, received July 24, and extracted July 25 and 26. Extraction occurred 6-9 days after sample collection. Analysis of carbofuran occurred within 20 days of collection, and for all other pesticides, occurred within 18 days of collection. Details on dates of collection, extraction, and analysis for each sample are shown in Appendix 1.

Whole water samples were analyzed for all pesticides, except carbofuran, as follows. A measured volume of 800 milliliters (ml) of a water sample was transferred to a one liter separatory funnel. Sufficient aqueous alkali was added to adjust the pH to 8. Pesticides were extracted by adding 75 ml of methylene chloride, shaking vigorously for two minutes, and then left standing for several minutes to allow separation of the water and solvent layers. The solvent layer was drained into a 500 ml Erlenmeyer flask. Each sample was extracted three times by the above method. The extracts were combined in the flask, transferred to a Kuderna-Danish apparatus in a hot water bath, and methylene chloride extract was concentrated to near dryness. The sample was then diluted to a final volume of 10 ml with hexane, and an internal standard was added.

The samples were subjected to analysis by gas chromatography with electron capture detection using dual megabore columns. The megabore columns were 30 meter glass columns packed with DB-5 and DB-608. Injector temperature was 220°C, and detector temperature was 300°C. The temperature program was initially held at 160°C for five minutes, increased at a rate of 5°C per minute to 180°C, held at 180°C for 10 minutes, increased at a rate of 10°C per minute to 220°C, and held for 15 minutes.

Analysis for carbofuran was conducted as follows. Samples were filtered through a 0.45 micron Millipore filter, then a 500 microliter aliquot was injected into a Waters Nova-Pak reverse phase high performance liquid chromatography (HPLC) column. Following elution from the HPLC column, carbamate analytes were hydrolyzed with aqueous sodium hydroxide. The methylamine formed during hydrolysis reacted with ortho-phthalaldehyde and 2-mercaptoethanol to form a highly fluorescent derivative, which was quantified by the HPLC's fluorescence detector.

Additionally, distilled water samples were spiked and analyzed to assess compound loss during storage prior to extraction. Three samples of distilled water were spiked with the seven pesticides

on the day the samples arrived at the laboratory. One day after arrival, one of the samples was extracted and analyzed as described above. The other two spiked samples were extracted and analyzed on three and nine days after arrival.

During water sample collection at each site, the following activities were also performed. Temperature, pH, dissolved oxygen, and conductivity were measured with a Surveyor(R) II Hydrolab, which was calibrated before and after field work. Photographs were taken at each site, and slides are archived at U.S. Fish and Wildlife Service, Annapolis Field Office. Observations of conditions such as waterway width, color, suspended sediment load, substrate type, flow; surrounding vegetation; and predominant land use were recorded.

RESULTS

Stream Conditions

Samples were collected July 18-22, 1990. Dates for collections at particular sites are listed in Appendix 1. Stream sampling location and observations on width, depth, and substrate are listed in Table 1. In general, larger streams were fairly turbid, as would be expected during this time of year when regular rainfall occurred.

Daily precipitation at National Oceanic and Atmospheric Administration station closest to sampling sites is shown in Appendix 2. Examination of monthly rainfall and deviation from long-term means showed that most counties were slightly (Harford and Cecil) to well (Kent and Baltimore) above average. An exception was Wicomico County, which was slightly below average. (National Oceanic and Atmospheric Administration 1990).

Physical conditions: temperature, pH, dissolved oxygen, and conductivity, are listed in Table 2. No temperature measurement seemed particularly high or low. The highest temperature recorded was 31.86°C at site 1 of Aydylotte Branch. No pH measurement was outside the range of 6.5 - 8.5 specified in MDE Water Quality Standards (COMAR 26.08.02.03-3), with one exception. Water from site 2 of Aydylotte Branch had a pH of 6.32. In general, dissolved oxygen levels in the streams were very good. Again, Aydylotte Branch had very low levels; dissolved oxygen at one site was below (3.70 milligrams per liter [mg/L]), and one was just above (5.29 mg/L) the MDE Water Quality Standard concentration of 5.0 mg/L. Morgan Creek also had a very low dissolved oxygen level of 2.02 mg/L. The Morgan Creek sampling site was just downstream of a small sewage treatment plant, which may have affected dissolved oxygen levels (Rosanna Kroll, MDE Standards and Certification Division, personal communication).

Table 1. Location and condition of sampling sites. Site numbers are not necessarily in order of upstream to downstream.

Stream County	Site	Location	Width (ft)	Depth (ft)	Substrate	Notes
Aydylotte Branch Wicomico	1	Rt. 136 crossing	5-10	0.5	n.r.	1
	2	Rt. 129 crossing	10	0.5	muck	2
Little Elk Creek Cecil	1	Rt. 545 crossing	45	1.5	rock, sand gravel	3
Little Northeast Creek, Cecil	1	Mechanic Valley Rd.	40-50	1	bedrock	
Octoraro Creek Cecil	1	Rowlands-ville Rd.	90	3	bedrock rock, gravel	
Morgan Creek Kent	1	Rt. 448 crossing	20	n.r.	mud	4
Langford Creek Kent	1	Langford Brices Mill Rd.	30	n.r.	mud, sand gravel	

n.r. - not recorded

Notes:

1 This was a stagnant drainage ditch surrounded by agriculture. An abnormal tadpole was observed.

2 Site was just upstream from the confluence with Burnt Mill Branch. This was a stagnant drainage ditch surrounded by agriculture, supporting some submerged aquatic vegetation.

3 A nearby sign warned that the stream was polluted.

4 Stream was slow moving and turbid.

Table 1 (cont.). Location and condition of sampling sites. Site numbers are not necessarily in order of upstream to downstream.

Stream County	Site	Location	Width (ft)	Depth (ft)	Substrate	Notes
Deer Creek Harford	1	Rt. 543 crossing	45	n.r.	rock	
	2	Rt. 161 crossing	90	2	sand to boulders	
	3	Rt. 165 crossing	30-45	2	rock	5
	4	Stafford Bridge	90	2-3	sand to boulders	6
Whitemarsh Run Baltimore	1	Rt. 1 crossing	2-4	0.5	sand and cobbles	7
	2	Rt. 40 crossing	30	1	sand	8
	3	Avondale Rd. bridge	2	0.5	sand and pebbles	9

n.r. - not recorded

Notes:

5 This was the most upstream site on Deer Creek, followed in a downstream direction by sites 1, 2, and 4. Turbidity increased from upstream to downstream. Land use around this site was almost exclusively corn fields.

6 This site was just upstream of the only known location of the Federally endangered Maryland darter (Etheostoma sellare).

7 Land use around this site is suburban and industrial.

8 Water was highly turbid at this site; land use is industrial.

9 Land use is suburban; creek is adjacent to major highway.

Table 1 (cont.). Location and condition of sampling sites. Site numbers are not necessarily in order of upstream to downstream.

Stream County	Site	Location	Width (ft)	Depth (ft)	Substrate	Notes
Honeygo Run Baltimore	1	Rt. 40 crossing	2-3	0.5	sand	
	2	Joppa Rd. crossing	2-3	0.5	sand to cobble	10
Monocacy River Frederick	1	Rt. 77 crossing	90	n.r.	rock and mud	11
	2	Rt. 26 crossing	180	n.r.	rock	
	3	Rt. 355 crossing	150	n.r.	gravel to rock	12
Owens Creek Frederick	1	Foxville Deerfield Rd.	4-5	n.r.	rock	13
Fishing Creek Frederick	1	Confluence of Little Fishing Creek	2-3	3	cobble rock	14
	2	see note	4-5	1	cobble rock	15

n.r. - not recorded

Notes:

10 Land use is suburban/rural with some agriculture.

11 Sites are in order upstream to downstream. Mud and puddles indicated a recent rain. Moderate turbidity was observed at all Monocacy river sites.

12 Land use included agriculture and industry.

13 Land use included forest, pasture, and row crops.

14 Control site, sample taken upstream of Fishing Creek Reservoir at stream gauge. Watershed is mostly forested.

15 Control site. An unnamed gravel road turns south off of Mountaindale Rd. and crosses Fishing Creek. The sample was taken here. Yards of single family houses lined one side of the stream; the other side was forested.

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Table 2. Physical conditions measured at streams during water sample collection. Site numbers are not necessarily in order of upstream to downstream.

Stream	Site	Time	Temperature (°C)	pH	DO[1] (mg/L)	Conductivity (µmhos)
Aydylotte Branch	1	1830	31.86	6.87	3.70	186
	2	1745	27.84	6.32	5.29	155
Little Elk Creek	1	1215	24.17	7.82	8.45	182
Little Northeast Creek	1	1250	24.07	8.07	8.94	157
Octoraro Creek	1	1350	26.20	8.02	8.63	196
Morgan Creek	1	1100	24.65	6.82	2.02	159
Langford Creek	1	1015	26.19	6.91	6.40	125
Deer Creek	1	1500	24.68	7.44	9.02	133
	2	1420	24.28	7.32	8.27	143
	3	1600	24.72	7.28	9.00	138
	4	1345	24.79	7.61	8.49	144
Whitemarsh Run	1	1030	23.39	7.53	7.97	326
	2	1220	25.67	7.37	7.62	260
	3	0945	22.18	7.37	7.17	526
Honeygo Run	1	1150	22.97	6.85	7.91	232
	2	1120	23.16	7.14	7.96	220
Monocacy River	1	1330	25.60	7.44	7.02	258
	2	1600	26.01	7.45	7.03	274
	3	1310	25.05	7.72	7.36	278
Owens Creek	1	1515	21.62	7.60	8.13	137
Fishing Creek	1	1100	18.11	7.01	8.61	28
	2	1145	22.45	7.25	8.19	40

1 DO - Dissolved oxygen

Sample Analysis

Six of seven pesticides were detected in one or more water samples (Table 3). Ranges of percent recovery in spiked samples and detection limits are shown in Appendix 3. In general, percent recovery using the extraction method previously described was very good, ranging from 86 to 130%. Simazine had the greatest range of recoveries (86 - 120%) and tended to have somewhat low percent recovery. Recoveries for cyanazine were consistent but high (120 - 130%). The limit of detection requested was 0.1 micrograms per liter (µg/L is equivalent to parts per billion). All pesticides had limits of detection which fell reasonably around this concentration with the exception of carbofuran, which was an order of magnitude higher (1.5 µg/L).

Water samples spiked to assess effects of storage indicated that six of the seven pesticides showed very little degradation over nine days. However, carbofuran had degraded to 55% recovery after nine days of storage (estimated from a single sample with no replication).

Pesticide Levels in Maryland Streams

Concentrations of the seven pesticides in stream water samples are reported in Table 3. Alachlor was detected only in the Monocacy River at levels ranging from 0.06 to 0.10 µg/L. Atrazine was detected in four streams: Octoraro Creek, Morgan Creek, Langford Creek, and all three sites on the Monocacy River, at levels ranging from 0.38 to 2.88 µg/L. Carbofuran was not detected in any of the 65 samples. Chlorpyrifos was detected in only one stream, Whitemarsh Run, in the two most downstream of three sites at concentrations of 0.07 µg/L. Cyanazine was detected in the same four streams as atrazine: Octoraro Creek, Morgan Creek, Langford Creek, and all three sites on the Monocacy River, at levels ranging from 0.14 to 2.62 µg/L. Metolachlor was the most frequently detected of the seven pesticides analyzed for in this study, occurring in nine of 12 streams sampled. Levels ranged from 0.17 to 1.10 µg/L. Simazine was found in two streams: Octoraro and Morgan Creeks, at levels ranging from 0.30 to 1.17 µg/L.

Of all streams sampled, the greatest number of pesticides were detected in the Monocacy River (the largest stream sampled). Samples from this river contained much higher concentrations of metolachlor and relatively high levels of other pesticides, compared to other streams (Table 3). These results suggest that sampling of larger streams would be appropriate if the goal of sampling were to determine the variety of pesticides in surface water. Morgan Creek and Langford Creek, both in Kent County, also contained a large number of pesticides.

Table 3. Levels of six pesticides detected in water of 12 streams in Maryland.

Stream County	Site	Replicate	Alachlor	Atrazine	Chlorpyrifos	Cyanazine	Metolachlor	Simazine
Aydylotte Branch Wicomico	1	1	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
		2	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
	2	1	n.d.	n.d.	n.d.	n.d.	0.19	n.d.
		2	n.d.	n.d.	n.d.	n.d.	0.16	n.d.
		3	n.d.	n.d.	n.d.	n.d.	0.16	n.d.
Little Elk Creek Cecil	1	1	n.d.	n.d.	n.d.	n.d.	0.18	n.d.
		2	n.d.	n.d.	n.d.	n.d.	0.21	n.d.
		3	n.d.	n.d.	n.d.	n.d.	0.21	n.d.
Little Northeast Creek Cecil	1	1	n.d.	n.d.	n.d.	n.d.	0.31	n.d.
		2	n.d.	n.d.	n.d.	n.d.	0.32	n.d.
		3	n.d.	n.d.	n.d.	n.d.	0.34	n.d.
Octoraro Creek Cecil	1	1	n.d.	0.38	n.d.	0.17	0.27	0.32
		2	n.d.	0.43	n.d.	0.21	0.26	0.30
		3	n.d.	0.38	n.d.	0.21	0.26	0.30
Morgan Creek Kent	1	1	n.d.	1.35	n.d.	2.41	0.68	0.84
		2	n.d.	0.94	n.d.	2.62	0.53	1.17
		3	n.d.	1.24	n.d.	2.49	0.70	0.96
Langford Creek Kent	1	1	n.d.	0.78	n.d.	1.82	0.36	n.d.
		2	n.d.	0.78	n.d.	1.90	0.42	n.d.
		3	n.d.	0.81	n.d.	1.90	0.49	n.d.

n.d. - not detected at detection limits

Table 3 (cont.). Levels of six pesticides detected in water of 12 streams in Maryland.

Stream County	Site	Replicate	Alachlor	Atrazine	Chlorpyrifos	Cyanazine	Metolachlor	Simazine
Deer Creek Harford	1	1	n.d.	n.d.	n.d.	n.d.	0.29	n.d.
		2	n.d.	n.d.	n.d.	n.d.	0.21	n.d.
		3	n.d.	n.d.	n.d.	n.d.	0.23	n.d.
	2	1	n.d.	n.d.	n.d.	n.d.	0.24	n.d.
		2	n.d.	n.d.	n.d.	n.d.	0.23	n.d.
		3	n.d.	n.d.	n.d.	n.d.	0.23	n.d.
	3	1	n.d.	n.d.	n.d.	n.d.	0.17	n.d.
		2	n.d.	n.d.	n.d.	n.d.	0.17	n.d.
		3	n.d.	n.d.	n.d.	n.d.	0.17	n.d.
	4	1	n.d.	n.d.	n.d.	n.d.	0.23	n.d.
		2	n.d.	n.d.	n.d.	n.d.	0.23	n.d.
		3	n.d.	n.d.	n.d.	n.d.	0.23	n.d.
Whitemarsh Run Baltimore	1	1	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
		2	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
		3	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
	2	1	n.d.	n.d.	0.06	n.d.	n.d.	n.d.
		2	n.d.	n.d.	0.07	n.d.	0.17	n.d.
		3	n.d.	n.d.	0.07	n.d.	0.17	n.d.
	3	1	n.d.	n.d.	0.07	n.d.	n.d.	n.d.
		2	n.d.	n.d.	0.07	n.d.	n.d.	n.d.
		3	n.d.	n.d.	0.07	n.d.	n.d.	n.d.

n.d. - not detected at detection limits

Table 3 (cont.). Levels of six pesticides detected in water of 12 streams in Maryland.

Stream County	Site	Replicate	Alachlor	Atrazine	Chlorpyrifos	Cyanazine	Metolachlor	Simazine
Honeygo Run Baltimore	1	1	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
		2	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
		3	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
	2	1	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
		2	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
		3	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
Monocacy River Frederick	1	1	0.10	2.88	n.d.	0.35	1.10	n.d.
		2	0.10	1.99	n.d.	0.46	1.08	n.d.
		3	0.10	2.49	n.d.	0.39	1.09	n.d.
	2	1	0.10	1.71	n.d.	0.34	1.03	n.d.
		2	0.10	1.80	n.d.	0.23	0.92	n.d.
		3	0.10	1.73	n.d.	0.18	0.86	n.d.
	3	1	0.06	0.86	n.d.	0.30	0.59	n.d.
		2	0.08	0.85	n.d.	0.14	0.57	n.d.
		3	0.06	0.74	n.d.	0.14	0.57	n.d.
Owens Creek Frederick	1	1	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
		2	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
		3	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
Fishing Creek Frederick	1	1	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
		2	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
		3	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
	2	1	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
		2	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
		3	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.

n.d. - not detected at detection limits

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Three streams contained no detectable levels of pesticides: Honeygo Run, Fishing Creek, and Owens Creek. The latter two were chosen to serve as controls. Fishing Creek is surrounded by forest and is an appropriate control for future studies. However, the land use near Owens Creek included some agriculture; this creek is not recommended as a future control site.

DISCUSSION

In general, levels of pesticides found in streams were well below levels known to cause toxicity to aquatic fauna. The exception was chlorpyrifos, which occurred at levels possibly causing acute or chronic toxicity to sensitive species. Pesticide levels detected in this study were not notably higher than levels measured in other monitoring studies. However, the timing of sample collection in mid-July probably produced results which underestimated maximum impacts, since peak pesticide concentrations probably occurred within the previous two months, and some pesticides may have been diluted or degraded below detection level. A more detailed discussion of each pesticide is provided below.

Alachlor

In general, alachlor levels measured in this study were similar to or lower than levels measured in other studies. In a study performed by Susquehanna River Basin Commission (SRBC), monthly samples were collected from Octoraro Creek in the summer of 1981. Alachlor occurred at levels up to 2.7 µg/L (EPA STORET database). During an intensive watershed investigation of Pequea Creek in Pennsylvania, alachlor was measured in whole water, during a year with below average precipitation. The maximum baseflow concentration was 0.2 µg/L, and maximum storm event concentration was 0.8 µg/L. Highest concentrations were measured in May when the herbicide is usually applied (Lietman et al. 1983). Water was sampled from the Rhode, Choptank, and Poplar Rivers over several months in 1976; only four samples contained alachlor at concentrations near the detection limit of 0.02 µg/L (Beane 1977). Sampling of tributaries and the mainstem of the Susquehanna River in June through September 1981, detected alachlor in 37 of 88 samples at concentrations ranging from 0.07 to 11 µg/L (Takita 1984).

It seems unusual that alachlor was found in only one stream when it was ranked among the four highest use pesticides in five of the six counties sampled (Maryland Department of Agriculture 1990). Also, alachlor has been characterized as moderately mobile in sandy and silty soils (Environmental Protection Agency 1987). However, one study estimated only 0.02% of alachlor applied to fields was accounted for in surface runoff (Beane 1977). Several potential factors may explain why alachlor was

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not found more frequently when it probably had a high use. Use levels may have changed since the last pesticide use survey in 1988. Application may have occurred earlier in the season, and detectable levels were no longer present. Degradation in water may be rapid. No information on half-life in water could be located by this study.

Toxicity of alachlor to several invertebrate and vertebrate species occurring in Maryland is shown in Table 4. In general, levels causing toxicity were several orders of magnitude higher than levels measured in this study.

Atrazine

Atrazine occurred in many of the streams sampled, reflecting its use rate which was high in most counties where stream sampling occurred (Maryland Department of Agriculture 1990). Atrazine levels were similar to those reported in other studies.

The West Virginia Department of Natural Resources sampled several rivers in 1984, and found atrazine levels ranging from 0.01 to 0.32 µg/L (EPA STORET database). Seven tributaries to the Potomac River in Frederick County, Virginia had atrazine levels of 0.08 to 0.82 µg/L in 1974 (EPA STORET database).

Atrazine in Pequea Creek, PA, under base-flow conditions, was usually less than 0.5 µg/L, but samples contained up to 2.1 µg/L in late July and August. Storm flow samples contained atrazine concentrations as high as 4.5 µg/L (Lietman et al. 1983). Near the head of the Rhode River, MD, samples of bulk water were collected twice a week, and atrazine concentrations ranged from 0.003 to 0.19 µg/L with a mean of 0.04 µg/L (Wu et al. 1980). In the Susquehanna River and tributaries, atrazine was detected in five of 88 samples at levels as high as 2.50 µg/L (Takita 1984). Atrazine did not exceed 5.5 µg/L and was generally in the range of 1 µg/L in the mainstem of Chesapeake Bay, and did not exceed 3.5 µg/L in western tributaries between 1976 and 1980 (Environmental Protection Agency 1983). Sampling in the summers of 1982 and 1983 to evaluate the presence of triazine herbicides in drinking water measured atrazine in untreated Patuxent River water at levels up to 5 µg/L (Glotfelty et al. 1986). Atrazine has been found as high as 140 µg/L in the microsurface layer of the Rhode River, MD, following post-spray rainfall events (Environmental Protection Agency 1983).

Levels of atrazine causing toxicity to Maryland invertebrate and vertebrate species for which tests have been conducted are shown in Table 5. Levels found in water samples were several orders of magnitude lower than levels causing toxicity.

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Table 4. Toxicity of alachlor to several aquatic organisms.

Species	Effect	Duration	Concentration (µg/L)	Ref.
Water flea *Daphnia magna*	EC50	48 hours	21,000	1
Chironomid worm *Chironomus plumosus*	EC50	48 hours	3,200	1
Rainbow trout *Oncorhynchus mykiss*	LC50	96 hours	2,400	1
Bluegill *Lepomis macrochirus*	LC50	96 hours	4,300	1
Fathead minnow *Pimephales promelas*	LC50	96 hours	5,000	2

References:

1 Mayer and Ellersieck 1986

2 Geiger et al. 1986

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Carbofuran

Two confounding factors may have contributed to the lack of detection of this pesticide. Carbofuran had the highest detection level of all pesticides analyzed, and was found to degrade when tested over nine days of storage. Samples were extracted seven to nine days after collection (Appendix 1). Sample handling and analysis methods may be responsible for lack of detection in this study. Toxicity levels for local aquatic species are well above the detection limit of 1.5 µg/L (Table 6).

Chlorpyrifos

Chlorpyrifos is registered by EPA for general use against household pests, and for control of pests on ornamental plants and turfgrass (Environmental Protection Agency 1984). The single stream in which chlorpyrifos was detected, Whitemarsh Run, is surrounded by urban development, including a large and relatively recent residential development downstream of Route 1. The likelihood of urban nonpoint source runoff of this pesticide is supported by the fact that it was not found at the most upstream site, and was not found at nearby Honeygo Run, where land use was more rural.

Chlorpyrifos was the only pesticide from this study which occurred at levels which might cause direct toxicity to aquatic life. Levels found in Whitemarsh Run were near the EPA freshwater acute criteria of 0.083 µg/L, and above the freshwater chronic criteria of 0.041 µg/L (Environmental Protection Agency 1986). Levels in Whitemarsh Run were closer to those causing toxicity (Table 7) than for all other pesticides examined in this study.

It should be noted that the detection limit of 0.06 µg/L is close to the EPA criteria levels and, therefore, is not low enough to enable adequate assessment of possible impacts to aquatic biota. When concentrations are close to detection limits, accuracy and reliability are reduced.

Cyanazine

Cyanazine occurrence corresponded well with county pesticide use. Cyanazine was among the four highest use pesticides in counties where it was detected in streams, and use was low or not listed for the counties where it was not detected (Maryland Department of Agriculture 1990).

Few studies assessing cyanazine levels in surface water were located for comparison. Cyanazine was found at levels ranging from below detection limits to 0.2 µg/L in major rivers sampled

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Table 5. Toxicity of atrazine to several aquatic organisms.

Species	Effect	Duration	Concentration (µg/L)	Ref.
Water flea *Daphnia magna*	LC50	48 hours	6,900	1
Scud *Gammarus fasciatus*	LC50	48 hours	5,700	1
Channel catfish *Ictalurus punctatus*	LC50	60-204 hr.	220-340	2
Spot *Leiostomus xanthurus*	LC50	96 hours	8,500	3
Bluegill *Lepomis macrochirus*	LC50	96 hours	15,000-50,000	4
Rainbow trout *Oncorhynchus mykiss*	LC50	96 hours	8,800-17,000	4
Fathead minnow *Pimephales promelas*	LC50	96 hours	15,000	1
Brook trout *Salvelinus fontinalis*	LC50	96 hours	4,900-6,300	1

References:

1 Macek et al. 1976

2 Birge et al. 1979

3 Ward and Ballantine 1985

4 Bathe et al. 1973

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Table 6. Toxicity of carbofuran to several aquatic organisms.

Specie	Effect	Duration	Concentration (µg/L)	Ref.
Water flea *Daphnia magna*	EC50	48 hours	48.0	4
Yellow perch	LC50	96 hours	147	1
Perca flavescens	LC50	96 hours	120-400	2
Channel catfish *Ictalurus punctatus*	LC50	96 hours	248	2
Fathead minnow *Pimephales promelas*	LC50	96 hours	872	2
Rainbow trout *Oncorhynchus mykiss*	LC50	96 hours	380	2
Brown trout *Salmo trutta*	LC50	96 hours	560	2
Bluegill	LC50	96 hours	240	2
Lepomis macrochirus	LC50	96 hours	80	3

References:

1 Johnson and Finley 1980

2 Mayer and Ellersieck 1986

3 Carter and Graves 1972

4 Johnson 1986

Table 7. Toxicity of chlorpyrifos to several aquatic organisms.

Species	Effect	Duration	Concentration (µg/L)	Ref.
Scud *Gammarus fasciatus*	LC50	96 hours	0.32	1
Water flea *Daphnia magna*	LC50	24 hours	0.4	2
Water flea *Daphnia pulex*	LC50	24 hours	0.17	2
Atlantic silverside *Menidia menidia*	LC50	96 hours	1.7	4
Striped bass *Morone saxatilis*	LC50	96 hours	0.58	3
Mummichog *Fundulus heteroclitus*	LC50	96 hours	4.65	4
Fathead minnow *Pimephales promelas*	LC50	96 hours	200	5
Rainbow trout *Oncorhynchus mykiss*	LC50	96 hours	1 - 51*	6
Channel catfish *Ictalurus punctatus*	LC50	96 hours	280	6
Bluegill *Lepomis macrochirus*	LC50	96 hours	1.7 - 4.2*	6

* Toxicity increased with increasing temperature.

References:

1 Sanders 1972

2 Siefert 1987

3 Korn and Earnest 1974

4 Thirugnanam and Forgash 1977

5 Geiger et al. 1988

6 Mayer and Ellersieck 1986

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by USGS since 1986, and in the Monongahela River at levels up to 0.017 during monitoring by EPA in 1989 (EPA STORET database).

Levels of cyanazine causing toxicity to Maryland invertebrate and vertebrate species for which tests have been conducted are listed in Table 8. Levels causing toxicity are several orders of magnitude higher than levels found in water samples.

Metolachlor

Metolachlor is clearly a pesticide of concern in Maryland streams. It was detected in all but one of the streams sampled, excluding controls. Few studies assessing metolachlor levels in surface water were located for comparison. Rivers in several states monitored by USGS over several years contained metolachlor at levels ranging from below detection limits to 0.2 µg/L (EPA STORET database). Levels of metolachlor (Table 9) causing toxicity to Maryland invertebrate and vertebrate species for which tests have been conducted were several orders of magnitude higher than levels found in water samples.

Simazine

Although detected in only two streams, relatively high levels in Morgan Creek indicate a need for this pesticide to be included in future monitoring. As with other herbicides, levels of simazine (Table 10) causing toxicity to Maryland invertebrate and vertebrate species for which tests have been conducted were several orders of magnitude higher than levels found in water samples.

Concentrations of simazine from this study were similar to or lower than those reported from other studies. Simazine concentrations in Pequea Creek, PA, were as high as 1.0 µg/L in both base flow and storm samples. Concentrations were highest in May through October, but remained relatively constant throughout the year (Lietman et al. 1983). Sampling in the summers of 1982 and 1983 to evaluate the presence of triazine herbicides in drinking water measured simazine in untreated Patuxent River water at up to 1.7 µg/L (Glotfelty et al. 1986).

Environmental Fate

In order to adequately assess effects of a pesticide on the environment, movement through and persistence in terrestrial, aquatic, and biological systems must be determined. Many of the issues necessary to assess environmental fate are reviewed below. Of the seven pesticides included in this study, atrazine has been relatively well researched. Results from atrazine research have been included as examples, however, these results cannot be

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Table 8. Toxicity of cyanazine to several aquatic organisms.

Species	Effect	Duration	Concentration (µg/L)	Ref.
Scud *Gammarus fasciatus*	LC50	96 hours	2,000	1
Channel catfish *Ictalurus punctatus*	LC50	96 hours	10,400 - 17,400	1
Fathead minnow *Pimephales promelas*	LC50	96 hours	16,300 - 21,300	1
Rainbow trout *Oncorhynchus mykiss*	LC50	96 hours	9,000	1
Bluegill	LC50	96 hours	22,500	1
Lepomis macrochirus	LC50	96 hours	20,300	2

References:

1 Johnson and Finley 1980

2 Mayer and Ellersieck 1986

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Table 9. Toxicity of metolachlor to several aquatic organisms.

Species	Effect	Duration	Concentration (ug/L)	Ref.
Water flea *Daphnia magna*	EC50	48 hours	23,500	1
Chironomid worm *Chironomus plumosus*	EC50	48 hours	3,800	1
Fathead minnow *Pimephales promelas*	LC50	96 hours	8,000	1

Reference:

1 Mayer and Ellersieck 1986

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Table 10. Toxicity of simazine to several aquatic organisms.

Species	Effect	Duration	Concentration (µg/L)	Ref.
Water flea *Daphnia magna*	LC50	48 hours	>10,000	1
Scud *Gammarus fasciatus*	LC50	96 hours	130,000	1
Striped bass *Morone saxatilis*	LC50	96 hours	250 - 180,000	2
Rainbow trout *Oncorhynchus mykiss*	LC50	96 hours	>100,000	1
Fathead minnow *Pimephales promelas*	LC50	96 hours	>10,000	1
Bluegill *Lepomis macrochirus*	LC50	96 hours	100,000	1
	LC50	96 hours	90,000	3

References:

1 Mayer and Ellersieck 1986

2 Wellborn 1969

3 Bathe et al. 1973

extrapolated to other pesticides, as each is unique in its properties. Rather, examples of atrazine research are included to emphasize the need for this type of study on each pesticide.

Most pesticides enter the aquatic environment in rainwater runoff from agricultural fields. Many researchers have established that highest levels of pesticides enter streams during storm events just after application (Muir et al. 1978, Frank and Sirons 1979). However, a study of Quebec watersheds determined that a major amount of atrazine, which can persist in soils for a year or more, was lost from fields during snow melt runoff (Muir et al. 1978). One study determined that atrazine can be atmospherically transported; rainwater contained up to 2.19 µg/L atrazine (Wu 1979). In general, about one percent of pesticides are lost from fields through surface water runoff (Wu 1980, Logan 1981). However, the tendency of each pesticide to associate with rainwater runoff under different soil conditions needs to be assessed so that elevated levels in aquatic ecosystems can be reduced or avoided.

Persistence must be considered to determine environmental effects such as the length of exposure for an aquatic organism. Length of exposure data is essential for determining toxicity. Atrazine has been found in streams throughout the year (Richard et al. 1975, Muir et al. 1978, Frank and Sirons 1979), probably due to its persistence in soil. Atrazine applied to ponds has also persisted in water and sediment throughout several studies of up to one year in length (Kadoum and Mock 1978, Klaassen and Kadoum 1979, Herman et al. 1986). Simazine showed a similar persistence of over one year in water and sediment (Mauck et al. 1976). Cyanazine and alachlor in an irrigation tailwater pit had declined to just at or below detection limits by August (Kadoum and Mock 1978). Carbofuran, an insecticide, has been shown to degrade rapidly in water. It was not detected 21-26 days after application to a farm pond (Klaassen and Kadoum 1979).

One way that pesticides "disappear" from the water is by degradation. Two important degradation pathways are chemical hydrolysis (breakdown by water) and biodegradation (metabolism by bacteria and other microorganisms). In most studies, only the parent compound is measured. There are several important reasons for measuring degradation products in addition to the parent compound.

Degradation products must be measured to accurately assess the total amount of pesticide in the water or other media. One study found deethylated atrazine to occur at about 10 to 50% of atrazine levels, and in some instances were at the same order of magnitude as atrazine (Muir et al. 1978). Measuring only the parent compound may result in significant underestimation of pesticide levels.

Persistence of degradation products and their effects on biota may be different than the parent compound. Some studies have indicated that deethylated atrazine may be more persistent than atrazine (Jones and Winchell 1984). Four species of submerged macrophytes showed similar responses to atrazine at several exposure levels, but had varied responses to degradation products (Jones and Winchell 1984). In general, deethylated and deisopropylated atrazine caused less reduction in photosynthesis, while hydroxyatrazine had little effect and even increased photosynthesis in one species. Photosynthesis by several species of algae and cyanobacteria, which was reduced upon exposure to atrazine, was unaffected or reduced to a lesser degree upon exposure to degradation products (Stratton 1984). However, degradation products of some pesticides cause more severe effects than the parent compounds. In the aquatic environment, biota will probably be exposed to several compounds simultaneously or sequentially. Laboratory tests with combinations of atrazine and degradation products produced synergistic, antagonistic, or additive effects to macrophytes depending on the particular combination (Stratton 1984). Knowledge of toxicity of degradation products is essential to assess effects on the aquatic ecosystem.

The actual mechanisms of degradation are also important in order to determine the relative amounts of particular degradation products which may occur in different habitats and environmental conditions. Atrazine in an estuarine system was found to degrade much more rapidly than in soil, and somewhat more rapidly than in freshwater tests (Jones et al. 1982). The main pathway of degradation was sorption to substrate, degradation to hydroxyatrazine, and then desorption to the water. Dealkylation by microorganisms appeared to be a minor pathway in this study. Factors affecting the redox potential of sediment, such as low oxygen, would slow degradation and allow greater exposure of aquatic organisms. The finding that atrazine rapidly degrades in estuarine systems, primarily to the relatively non-toxic hydroxyatrazine, allowed the authors to postulate a lesser effect of atrazine on this habitat. Information such as this invites additional speculation. It might be inferred that atrazine in high flow streams with little sediment would degrade more slowly than in waters with muddy bottoms.

For each pesticide, degradation rates, tendencies to degrade by different pathways under different conditions, and toxic effects of degradation products need to be assessed. Extrapolation of results between even closely related pesticides is ill-advised.

Information regarding the propensity of a chemical to bioaccumulate is helpful in judging its persistence and potential to affect organisms at upper trophic levels. The bioaccumulation potential for six of the seven pesticides is very low with bioaccumulation factors (BAF), based on studies or

chemical/physical properties, of less than 35. Chlorpyrifos has a much stronger tendency to bioaccumulate, with reported BCFs of 630 - 2750 (Maryland Department of Environment 1989). In several studies, atrazine and simazine did not bioaccumulate in biota over time; residue levels in biota remained proportional to water levels (Mauck et al. 1976, Klaassen and Kadoum 1979, Lynch et al. 1982). Organisms rapidly absorbed atrazine, but reached equilibrium within one day (Klaassen and Kadoum 1979, Cossarini-Dunier et al. 1988). For carp, equilibrium was reached in less than 20 minutes in organs with high blood circulation, and depuration through gills and feces started as soon as 30 minutes following feeding of atrazine-treated pellets (Cossarini-Dunier et al. 1988).

Environmental Effects

Herbicide levels measured in this study were well below those known to cause acute toxicity to aquatic fauna in laboratory tests. However, chronic lethality and more subtle long term effects of these pesticides (such as effects on population, growth and reproduction, or effects on complex aquatic environments such as decreases in productivity) are not yet well characterized. Results of atrazine research will be reviewed here to point out some of the possible sublethal and community level responses which may be just as damaging to the aquatic ecosystem as direct toxicity. As in the previous section, atrazine results should not be extrapolated to other pesticides, but are reviewed here to point out the types of studies which need to be conducted for each pesticide to fully characterize its effect on the aquatic environment.

Although herbicides are relatively nontoxic to fauna, toxicity to photosynthetic organisms could affect the food chain by decreasing productivity. Changes in productivity can be measured as changes in biomass or photosynthesis (measured as oxygen production, chlorophyll level, or carbon fixation). Effects to algae, phytoplankton, and macrophytes are reviewed in the next three paragraphs.

Plumley and Davis (1980) tested effects of atrazine on salt marsh edaphic algae in laboratory cultures, microecosystems, and field enclosures. In the laboratory, no effects were detected at 22 µg/L, photosynthesis rate was reduced at 220 µg/L, and photosynthesis rate, chlorophyll level and cell number were reduced at 2200 µg/L. Microecosystem tests showed some reduction in primary productivity and enclosures showed reduced carbon fixation at 2000 µg/L. Finally, a safe level was established for atrazine in salt marsh ecosystems: 10 µg/L. Growth of several species of algae has been tested in the laboratory, and results ranged from stimulated growth to maximum inhibition at 20 µg/L. Photosynthesis of some species of algae was inhibited at atrazine concentrations as low as 1 µg/L (Torres and O'Flaherty 1976,

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Butler et al. 1975). A laboratory test using a mixture of organisms, dominated by Spirogyra and including many other algal species, flagellates, protozoans, and nematodes, recorded decreased oxygen production at 50 µg/L (Brockway et al. 1984). Biomass of periphyton in enclosures had not recovered to control levels one year after exposure to 100 µg/L atrazine (Herman et al. 1986).

Phytoplankton exposed to 20 and 500 µg/L atrazine in ponds showed a decrease in biomass and carbon fixation (deNoyelles et al. 1982). Recovery to control levels occurred by day 7 in the 20 µg/L groups, but the 500 µg/L ponds did not recover over 136 days. Phytoplankton exposed to as low as 1 µg/L have shown statistically significant reduction (3.4 - 4.3%) in photosynthetic rates in laboratory tests.

Atrazine concentrations of 5 to 10 µg/L have reduced photosynthesis in various species of submerged macrophytes (Forney and Davis 1981, Kemp et al. 1982, Jones et al. 1982). Plants exposed to low concentrations of atrazine showed a rapid decrease in photosynthesis, followed by gradual recovery. The higher the initial exposure, the longer the recovery time. Plants exposed to 10-15 µg/L took two to five weeks to recover, and plants exposed to 50 µg/L showed severe and persistent loss of productivity (Environmental Protection Agency 1983).

Because organisms have differing sensitivities to contaminants, changes in community structure may occur. A study examining the effects of atrazine on periphyton recorded almost complete disappearance of Cyanophyta (blue-green algae) at 100 µg/L (Herman et al. 1986). Dominant plankton species in ponds rapidly declined following exposure to 500 µg/L atrazine and were replaced by resistent species who made up 95% of remaining biomass by 15 days after application (deNoyelles et al. 1982). The same resistent species increased to only 50% of biomass in 20 µg/L exposure. The authors speculated that biomass decline was not only due to direct toxicity of atrazine, but also to inability of sensitive species to recover from grazing pressure by zooplankton.

Reduction in productivity and biomass in photosynthetic organisms demonstrated in the above paragraphs can result in effects to organisms higher in the food chain. Zooplankton biomass in ponds was reduced following a reduction in phytoplankton biomass due to atrazine exposure at 500 µg/L (deNoyelles et al. 1982). Aquatic insect emergence in the same ponds was studied, and several species showed significantly lower emergence rates in ponds treated with 20 µg/L atrazine (Dewey 1986). Declines in insect species richness were related to reductions in nonpredatory species at 20 µg/L while predatory species showed no atrazine-related changes up to 500 µg/L, probably indicating an effect due to reduction in food (periphyton and macrophytes) rather than

toxicity. Several species of nonpredatory aquatic insects emerged significantly earlier relative to control ponds, which may have been a response to reduced food availability. Bluegills from ponds treated with 20 and 500 µg/L had significantly fewer prey items in their stomachs, and prey consisted of significantly fewer taxonomic groups than controls (Kettle et al. 1987). While pesticides can affect organisms by reducing the food supply in general, particular species with specialized diets can also be affected if their prey is especially sensitive to the pesticide.

Secondary effects may cause changes or damages not directly attributed to toxicity. After exposure to atrazine (20 - 500 µg/L), rapid increases in biomass of resistent phytoplankton species may have been in partial response to reduced grazing pressure when zooplankton declined from reduced food supply (deNoyelles et al. 1982). Reproduction of bluegills in ponds treated with atrazine (20 µg/L) was significantly less than controls (Kettle et al. 1987), but previous laboratory results indicated toxicity was unlikely. Reduction of bluegill young in atrazine treated ponds may have been related to increased predation of adult bluegill on eggs and young due to lack of insect prey. Also, almost complete absence of macrophytes in these ponds may have reduced hiding places for young bluegills, resulting in increased probability of predation.

Studies examining productivity changes, community level changes, and secondary effects are much more effective than laboratory toxicity tests in determining impacts of pesticides on aquatic ecosystems. However, almost none of these studies addressed effects from pulsed exposure. Aquatic biota may be exposed to pesticides after every sizeable rainfall during the summer. Herman et al. (1986) found very few changes to periphyton in an enclosure during an initial exposure to 100 µg/L atrazine. A second application raised atrazine levels 20-30% and resulted in decreased chlorophyll levels, carbon fixation, and biomass of remaining periphyton. In another study, recovery of submerged plant photosynthesis to control levels was based on atrazine exposure level. Major impacts to plants could occur if intervals between exposure were less than plant recovery time, particularly in association with stresses due to decreases in light available to the plants due to turbidity (Environmental Protection Agency 1983). The issues of frequency of pesticide pulses in streams and effects of pulses on aquatic biota need to be addressed.

CONCLUSIONS

In light of the above discussion, we conclude the following. Chlorpyrifos is clearly of concern because of its occurrence at levels likely to cause acute or chronic toxicity, and its

tendency to bioaccumulate. Chlorpyrifos occurred in one of two streams surrounded by urban land use, suggesting that additional streams of this type should be monitored.

Carbofuran was not detected in any sample, possibly due to problems with sample storage and analysis. Because carbofuran has a relatively high toxicity and use level in Maryland, additional monitoring including rapid analysis and lower detection limits is necessary to confirm whether this pesticide is of concern.

Concentrations of the five herbicides were probably underestimated because of timing of sample collection late in the cycle of agricultural application and lack of analysis of degradation products, which can account for a significant amount of total pesticide. Even during peak runoff periods and including measurement of degradation products, pesticides would probably not occur at levels likely to cause direct toxicity to fauna. Effects on photosynthetic organisms and productivity, and secondary effects to aquatic food chains have been documented for atrazine, and may be occurring at levels found in this study. In order to determine whether effects are occurring for other herbicides, similar studies would have to be performed, and should include effects of degradation products and pulsed exposure. Also, aquatic biota may also be simultaneously or sequentially exposed to more than one pesticide, other pollutants, and physical conditions such as high turbidity which cause additional stress. Not enough research has been conducted to adequately assess effects on the aquatic environment due to pesticide levels measured in this study. Research on metolachlor should be particularly emphasized because of its ubiquitous occurrence in the streams sampled.

Large amounts of time and money are required for these types of research. We suggest an alternative solution. Elimination of a possible problem is preferable to determining the degree of the problem. Farmers should be encouraged to use best management practices which reduce both the amount of pesticides used and the amount of runoff into aquatic systems.

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RECOMMENDATIONS

Monitoring

Monitoring at sample sites over time should be done to determine peak pesticide concentrations, length of pesticide occurrence, and pulsed aspect of occurrence in order to assess effects to biota.

Monitoring should focus on watersheds to allow comparison of pesticide levels in water with pesticide use patterns and rainfall events.

Analysis should include degradation products to determine total pesticide levels.

Monitoring for chlorpyrifos in White Marsh Run and other streams in urban areas should be conducted.

Monitoring of carbofuran should continue with rapid sample analysis and appropriate detection limits.

Monitoring of Morgan Creek in Kent County and Monocacy River in Frederick County should be continued as they contained particularly high levels of pesticides relative to other sites.

Research

Toxicity of pesticide degradation products should be determined.

Research should be focused on effects to photosynthetic organisms, plant community structure, and algae/zooplankton dynamics from exposure to herbicides at levels of 1-50 µg/L.

The effects of repeated exposure to low levels of pesticides need to be ascertained.

Of the herbicides of concern, research should be focused first on metolachlor because of its ubiquitous occurrence in Maryland streams.

Research is needed on laboratory methodology to provide lower detection limits for chlorpyrifos.

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Appendix 1. Dates of sample collection, extraction, and analysis, 1990, and age of samples at extraction and analysis.

Stream	Site	Date Coll.	Date Extr.	Sample Age at Extr.	Date GC Anal.	Sample Age at GC Anal.	Date LC Anal.	Sample Age at LC Anal.
Aydylotte Branch	1	7/20	7/25	5 days	8/02	13 days	8/04	15 days
	2	7/20	7/25	5 days	8/02	13 days	8/04	15 days
Little Elk Creek	1	7/19	7/25	6 days	8/02	14 days	8/04	16 days
Little Northeast Creek	1	7/19	7/25	6 days	8/02	14 days	8/04	16 days
Octoraro Creek	1	7/20	7/25	5 days	8/03	14 days	8/04	15 days
Morgan Creek	1	7/20	7/25	5 days	8/03	14 days	8/04	15 days
Langford Creek	1	7/20	7/25	5 days	8/03	14 days	8/04	15 days
Deer Creek	1	7/19	7/25	6 days	8/03	15 days	8/04	16 days
	2	7/19	7/25	6 days	8/03	15 days	8/04	16 days
	3	7/19	7/25	6 days	8/03	15 days	8/04	16 days
	4	7/19	7/25	6 days	8/03	15 days	8/04	16 days
Whitemarsh Run	1	7/19	7/25	6 days	8/03	15 days	8/04	16 days
	2	7/19	7/25	6 days	8/03	15 days	8/05	17 days
	3	7/19	7/25	6 days	8/03	15 days	8/05	17 days
Honeygo Run	1	7/19	7/25	6 days	8/04	16 days	8/05	17 days
	2	7/19	7/25	6 days	8/04	16 days	8/06	18 days
Monocacy River	1	7/18	7/26	8 days	8/04	17 days	8/06	19 days
	2	7/18	7/26	8 days	8/04	17 days	8/06	19 days
	3	7/22	7/26	4 days	8/04	13 days	8/06	15 days
Owens Creek	1	7/18	7/26	8 days	8/04	17 days	8/06	19 days
Fishing Creek	1	7/18	7/26	8 days	8/04	17 days	8/06	19 days
	2	7/18	7/26	8 days	8/04	17 days	8/06	19 days

GC - Gas chromatography analysis for all pesticides except carbofuran.
LC - Liquid chromatography analysis for carbofuran.

Appendix 2. Precipitation (inches) at weather stations near sampling sites.

Date (July)	Salisbury Airport (AB)	Newark DE Univ. Farm (LE LN OC)	Chester-town (MO LA)	Cono-wingo Dam (DE)	Towson (WM HG)	Frederick Police Barracks (MR)	Catoctin Mountain Park (OW FI)
1	0.11		0.48	0.25		0.17	0.37
2				0.06			
3							
4							
5	0.22	1.95	0.15	0.12		0.13	0.69
6		0.06		0.01			0.02
7					0.50		
8				0.09			
9			0.58	0.14			
10	0.84	0.32	1.47	0.32	0.67		0.02
11	0.11	0.29	0.02	0.80	1.27	0.16	0.60
12	0.39	0.02	1.62	1.32	0.20	0.14	0.23
13	0.01	1.36	0.33	0.10	2.20	2.00	1.23
14	0.06	0.56	0.05	0.38	1.28	0.10	0.53
15		0.20	0.05	0.43	0.06	1.95	0.45
16			0.04				0.39
17							
18							
19							
20			0.17				
21		0.12	0.09	0.36	0.05	1.17	0.23
22				0.09	0.14	0.05	1.07
23		0.27	Trace	0.11	0.32	0.28	0.05

AB - Aydylotte Branch
LE - Little Elk Creek
LN - Little Northeast Creek
OC - Octoraro Creek
MO - Morgan Creek
LA - Langford Creek
DE - Deer Creek
WM - Whitemarsh Run
HG - Honeygo Run
MR - Monocacy River
OW - Owens Creek
FI - Fishing Creek

Appendix 3. Percent recovery in spiked samples and limits of detection for seven pesticides.

Pesticide	Percent Recovery (%)	Limit of Detection (µg/L)
Alachlor	100	0.06
Atrazine	90 - 120	0.38
Carbofuran	92 - 100	1.5
Chlorpyrifos	93 - 97	0.06
Cyanazine	120 - 130	0.14
Metolachlor	100 - 110	0.15
Simazine	86 - 120	0.30